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# 含钒三元氧化物纳米晶体的制备、表征及应用

# Synthesis, Characterization and Applications of Ternary Oxides Nanocrystal Containing Vanadium Ion

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# Synthesis, Characterization and Applications of Ternary Oxides Nanocrystal Containing Vanadium Ion

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# 摘 要

钒基化合物作为一类多功能性材料，在光、电、磁、热、力等领域呈现出独特的性质和潜在的应用前景；而且，我国钒储量占全球钒储量的19%，居世界第三。所以，充分开发利用钒资源，对钒基化合物的合成方法探索及性能研究引起了研究学者的高度重视。本论文主要采用水/溶剂热方法合成钒基氧化物纳米材料及其掺杂纳米材料（$Zn_{3-3x}M_{3x}V_2O_7(OH)_2(H_2O)_2$, $Zn_{3-3x}M_{3x}V_2O_8$, $BiVO_4$），通过改变实验条件对产物形貌、尺寸和组分等进行有效控制合成，并探索产物在锂离子二次电池、光催化降解污染物方面的应用。主要研究内容和结果如下：

1. 以氧化锌和五氧化二钒为原料，以 CTAB 为表面活性剂，通过水热法合成了片状和片花状的 $Zn_3V_2O_7(OH)_2(H_2O)_2$。利用 XRD、SEM、TEM 等手段对所制备的样品进行了表征，实验结果表明 $Zn_3V_2O_7(OH)_2(H_2O)_2$ 是由主晶面为{0001}面的纳米片组成。初步研究了各形貌 $Zn_3V_2O_7(OH)_2(H_2O)_2$ 颗粒的电化学性能和光催化性能，结果表明片花状 $Zn_3V_2O_7(OH)_2(H_2O)_2$ 表现出优良的光催化性能及电化学性能。与其它形貌样品相比，片花状 $Zn_3V_2O_7(OH)_2(H_2O)_2$ 由于具有相对较大的比表面积，在 100 min 时的降解效率达 91%；在 0.02～3.0 V 的电位区间，0.2 A/g 电流密度下的室温恒流充放电循环测试中，具有 3D 分级结构片花状形貌的 $Zn_3V_2O_7(OH)_2(H_2O)_2$ 首圈比容量为 882.1 mAh/g，循环 100 圈后仍保持 667.2 mAh/g 的比容量，表现出优良的循环稳定性。

2. 通过简单的水热法合成了过渡金属离子掺杂焦钒酸锌/钒酸锌，通过 XRD、SEM、BET 等技术对其进行表征，并对 XRD 图的谱峰进行拟合计算。首次对得到的几种不同掺杂样品的光催化性质和电化学性质进行了测试和比较。实验结果表明：经 450 ℃煅烧得到的 0.1 at.% Cu 掺杂 $Zn_3V_2O_8$ 纳米颗粒对亚甲基蓝（MB）的可见光催化降解效果最好；而在锂离子二次电池的测试中，5.0 at.% Fe 掺杂 $Zn_3V_2O_7(OH)_2(H_2O)_2$ 的电化学性能最优。

3. 在水热、溶剂热或沉淀法条件下，合成了不同形貌的 m-$BiVO_4$。通过 pH 的调节，有效调控了类梭状 m-$BiVO_4$ 的尺寸。具有不同形貌的颗粒在可见光范围内都具有一定的光催化活性，与分级结构的梭状 m-$BiVO_4$ 颗粒相比，主要以

{001}面裸露的 m-$BiVO_4$ 纳米片对 MB 的光催化降解效率最高，光照 20 min 内对 MB 的降解效率可达 83.1%, 原因是因为{001}面具有较高的表面活性。

**关键词：**三元钒氧化物；纳米材料；掺杂；锂离子二次电池；光催化

# Abstract

Vanadium compounds, as an important multifunctional material, have potential applications in optical, magnetic, electric, thermodynamic and mechanical fields due to the unique properties. The reserve of vanadium in China accounts for 19%, which ranks the third in the world. To effectively utilize vanadium resource, the studies on the design and synthesis of nano-materials based on vanadium compounds have been attracted extensive attention. In this thesis, vanadium compounds and their doped materials ($Zn_{3-3x}M_{3x}V_2O_7(OH)_2(H_2O)_2$, $Zn_{3-3x}M_{3x}V_2O_8$, $BiVO_4$) were synthesized by hydro/solvothermal method, their morphologies, sizes and compositions were controlled successfully, and the products were further investigated for their potential use as anode materials for Li-ion rechargeable battery, and as photocatalysts to degrade organic pollutant. The main contents and results were summarized as follows:

1. $Zn_3V_2O_7(OH)_2(H_2O)_2$ micro/nanostructures with different morphologies were hydorthermally synthesized by using zinc oxide and vanadium pentoxide as starting materials and cetyltrimethyl ammonium bromide as surfactant. The as-prepared products were characterized by means of XRD, SEM, BET and TEM. Experimental results indicated that $Zn_3V_2O_7(OH)_2(H_2O)_2$ microstructures were assembled with nanoplates which mainly exposed of {0001} crystal facets. Photocatalytic properties of $Zn_3V_2O_7(OH)_2(H_2O)_2$ and their potential applications as anode materials for Li-ion rechargeable batteries were studied by photocatalytic degradation tests towards methylene blue and electrochemical tests, respectively. It could be found that the flowerlike $Zn_3V_2O_7(OH)_2(H_2O)_2$ microparticles showed good photocatalytic performance and electrochemical performance. The degradation efficiency of $Zn_3V_2O_7(OH)_2(H_2O)_2$ microflower was 91% within 100 min because of relatively large specific surface area; $Zn_3V_2O_7(OH)_2(H_2O)_2$ microflower electrode exhibited a high discharge capacity of 882.1 mAh/g in the first cycle and still retained 667.2 mAh/g after 100 cycles at a current density of 0.2 A/g within a potential window of

0.02～3.0 V, which could be attributed to its 3D hierarchical structure.

2. Transition metal ions doping $Zn_3V_2O_7(OH)_2(H_2O)_2$/$Zn_3V_2O_8$ were synthesized via a hydrothermal route. The phase and morphology of the as-prepared samples were characterized by means of XRD, SEM and BET, and profile fitting was operated through X'pert Highscore procedure. It was the first time that transition metal ions doping $Zn_3V_2O_7(OH)_2(H_2O)_2$/$Zn_3V_2O_8$ were used as the photocatalysts under visible light irradiation and the anode for Li-ion rechargeable batteries. It was found that at 450 ℃, 0.1 at.% Cu doped $Zn_3V_2O_8$ exhibited the highest photocatalytic activity for visible degradation of methylene blue (MB) among the doping and undoping analogues and that 5.0 at.% Fe doped $Zn_3V_2O_7(OH)_2(H_2O)_2$ improved the electrochemical performance of the materials.

3. The m-$BiVO_4$ nanoparticles with different morphologies were synthesized via hydrothermal, solvothermal or precipitated method. The sizes of the spindlelike m-$BiVO_4$ were effectively controlled by adjustment of pH values. The photocatalytic properties of the as-prepared m-$BiVO_4$ particles were investigated. The results indicate that m-$BiVO_4$ nanoplates which mainly exposed of {001} facets exhibit highest photocatalytic degradation efficiency towards MB among all as-prepared samples. Its photocatalytic degradation efficiency towards MB reached 83.1% within 20 min because of higher activity of {001} crystal facets.

**Keywords：** Ternary vanadium oxide; Nanomaterials; Dopping; Li-ion rechargeable battery; Photocatalytic properties